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IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :

SATOSHI MARUYAMA, ET AL.

EXAMINER: CANTELMO, G.

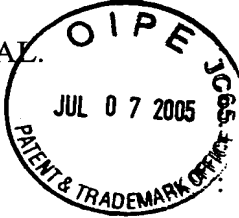
SERIAL NO: 10/002,979

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FOR: ELECTRODE COMPOSITION AND :
LITHIUM SECONDARY CELL



DECLARATION UNDER 37 C.F.R. § 1.132

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

I, Satoshi Maruyama, declare and state as follows:

1. I am a named co-inventor in the above-identified application.
2. I was born on June 17, 1955. I graduated from University of Tokyo, Faculty of engineering, with a master of engineering in 1980. I was employed by TDK Co., on March, 1987, and since 1987 I had been a member of TDK R&D Center. Since August 1995, I had been engaged in research and development of electrochemical devices up to the present time.
3. I am familiar with the claims, and have read the Office Action mailed April 6, 2004, in the above-identified application.

4. In order to exhibit that the combination of “ γ -butyrolactone” and “PVDF homopolymer obtained by emulsion polymerization process” produces unexpected results, the following experiments were conducted either by me or under my direct supervision.

Experiments:

Four kinds of battery, i.e. Example X-1 and Comparative Example Z-1, Z-2 and Z-3 were obtained.

Example X-1

Cathode:

LiCoO₂ as the cathode active substance, acetylene black as the conducting aid, and PVDF homopolymer (Kynar 741) as the binder were weighed in such a way as to give a ratio of LiCoO₂:acetylene black:PVDF homopolymer = 83:6:11 by mass. The PVDF homopolymer (Kynar 741) was product of Elf. Atochem Co., Ltd. (Atofina Co., Ltd.) and this PVDF homopolymer has been obtained by the emulsion polymerization process. Then, acetone was added in such a way as to give a ratio of acetone:PVDF homopolymer = 9:1 by mass. These were mixed together at room temperature to obtain cathode slurry.

Anode:

Mesocarbon microbeads (MCMB) as the anode active substance, and acetylene black as the conducting aid and PVDF homopolymer (Kynar 741) as the binder were weighed in such a way as to give a ratio of MCMB:acetylene black:PVDF homopolymer = 85:3:12 by mass. Then, acetone was added in such a way as to give a ratio of acetone:PVDF homopolymer = 9:1 by mass. These were mixed together at room temperature to obtain anode slurry.

The thus obtained cathode and anode slurries were each coated by a doctor blade process on a PET film, and the acetone was then evaporated off at room temperature to obtain a cathode and an anode.

Microporous film (separator):

Twenty (20) parts by weight of PVDF homopolymer (Kynar 761 made by Elf-Atochem Co., Ltd.) were dissolved in a mixed solution comprising 40 parts by weight of dimethylacetamide and 40 parts by weight of dioxane, and the resulting solution was then cast by a doctor blade process on a glass sheet at a thickness of 200 μ m.

Immediately after the casting, the glass sheet was dipped in a solidifying bath comprising 80 parts by weight of dioxane and 20 parts by weight of water for 10 minutes for solidification, then the glass sheet was washed in a water stream for 30 minutes, and then dried at 60°C for 1 hour, thereby obtaining a microporous film having a thickness of 50 μ m and comprising a poly(vinylidene fluoride) homopolymer.

The microporous film was found to have a porosity of 70% and a pore diameter of 0.2 μ m.

Electrolyte solution:

LiBF₄ as electrolyte was solved in solvent mixture of ethylene carbonate (EC) and γ -butyrolactone (EC: γ -butyrolactone = 3:7 by volume). The concentration of the electrolyte was set to 1 mol/L.

Assembly:

The cathode, the microporous film and the anode were each cut to given size, and the resultant sheets were heat-laminated together at 130 to 160°C to form a battery assembly.

Then, an aluminum grid with a conductive adhesive coated ahead thereon as a collector was heat-laminated on the cathode while a copper grid with a conductive adhesive coated ahead thereon as a collector was heat-laminated on the anode.

Subsequently, the battery assembly was impregnated with the electrolyte solution, and then sealed in an aluminum laminated pack to obtain a lithium secondary battery (BF system).

Comparative Example Z-1

Comparative Example Z-1 was conducted under the same condition of Example X-1 except for the binder. The PVDF homopolymer (KF1000, Kureha) was used as the binder of the cathode and the anode. This PVDF homopolymer has been obtained by suspension polymerization.

Comparative Example Z-2

Comparative Example Z-2 was conducted under the same condition of Example X-1 except for the solvent in electrolyte solution. The mixture of EC and diethylene carbonate (DEC) (EC: DEC = 3:7 by volume) was used as the solvent.

Comparative Example Z-3

Comparative Example Z-3 was conducted under the same condition of Comparative Example Z-1 except for the solvent in electrolyte solution. The mixture of EC and DEC (EC: DEC = 3:7 by volume) was used as the solvent.

Evaluation:

The batteries were charged under the following conditions: constant current-constant voltage charging was applied, the upper limit voltage was 4.2V, and the charging current was set to the value that the charging was completed at almost one hour. Then, the battery was measured for its post-charging capacity. Moreover, “the rate of capacity decrease” is obtained by the equation of (the post charging capacity)/(reference post-charging capacity of PF (LiPF₆) system battery (230mAh)).

The reference PF system battery was the same as the BF (LiBF₄) system battery in Example Z-1 except for solvent (EC:DEC = 3:7 by volume) and electrolyte (LiPF₆) in electrolyte solution.

The results of the above examples were summarized in Table 1.

Table 1

	solvent in electrolyte solution	binder	capacity (mAh)	rate of capacity decrease (%)
Example X-1	EC+ γ -butyrolactone	PVDF homopolymer obtained by <u>emulsion</u> polymerization	218	5.2
Comparative Ex. Z-1	EC+ γ -butyrolactone	PVDF homopolymer obtained by <u>suspension</u> polymerization	202	13.7
Comparative Ex. Z-2	EC + DEC	PVDF homopolymer obtained by <u>emulsion</u> polymerization	205	10.9
Comparative Ex. Z-3	EC + DEC	PVDF homopolymer obtained by <u>suspension</u> polymerization	206	10.4

Example X-1, i.e. the combination of “ γ -butyrolactone” and “PVDF homopolymer obtained by emulsion polymerization” produces a higher capacity (the rate of capacity decrease) than others.

Example X-1 and Comparative Example Z-1 show that manufacturing process of binder strongly affects the capacity (the rate of capacity decreases) of the batteries whose

solvent has γ -butyrolactone. However, Comparative Example Z-2 and Z-3 show that manufacturing process of a binder does not affect the capacity (the rate of capacity decreases) of the batteries whose solvent does not have γ -butyrolactone.

5. In my opinion, based on the above data, the combination of “ γ -butyrolactone” and “PVDF homopolymer obtained by emulsion polymerization” produces unexpected results over the applied prior art.

6. The undersigned declares further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing therefrom.

7. Further declarant saith not.

丸山 哲
Signature Satoshi MARUYAMA
2005年6月30日
Date June 30, 2005